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THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES

Final Report

Harry R. Allcock

June 13, 1988

U. S. ARMY RESEARCH OFFICE

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PROBLEM STUDIED

The objective of this work was the synthesis and evaluation of new polymers derived from the inorganic elements. Specifically, the goal was to develop new methods of synthesis for polyphosphazenes and to develop an understanding of the ways in which changes in molecular structure alter the properties of the polymers and allow improved polymers to be designed.

SUMMARY OF THE MOST IMPORTANT RESULTS

First, a method has been developed for the synthesis of new polyphosphazenes with cyano side groups, and these have been used as precursors for the construction of organic side groups derived from the phosphazenenitrile structure. The new polymers are expected to be useful as new films and elastomers.

Second, a number of new classes of cyclo- and polyphosphazenes have been prepared that incorporate transition metals, such as iron, ruthenium, chromium, or cobalt into the organometallic side group structure. These macromolecules are hybrid polymer-metal materials, some of which combine the properties of organic polymers with those of metals. Typical of these materials are polyphosphazenes with ferrocene units as side groups. These show semiconductor properties and unusual oxidation-reduction behavior.

Third, a series of small molecule linear phosphazenes have been prepared that serve as synthetic and structural models for the high polymers. X-Ray diffraction structure studies and theoretical analysis of the results have helped to predict ways in which the properties of the analogous polymers can be changed in order to optimize properties that are needed for advanced engineering uses.

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LIST OF PUBLICATIONS

Electronic Properties of Phosphazene Substituents on Ferrocene R. A. Saraceno, G. H. Riding, H. R. Allcock, and A. G. Ewing J. Am. Chem. Soc. 1988, 110, 980-982.

The Current Status of Polyphosphazene Chemistry
H. R. Allcock
Chapter in "Inorganic and Organometallic Polymers", (eds. M. Zeldin, K. J. Wynne, and H. R. Allcock)
ACS Symp. Ser. 360, 1988, 250-267.

Transition Metal Derivatives of Polyphosphazenes: Synthesis of Polyphosphazenes and Cyclic Model Compounds with Iron Cyclopentadienyl Carbonyl Side Groups
H. R. Allcock, M. N. Mang, G. S. McDonnell, and M. Parvez

Macromolecules 1987, 20, 2060-2067

Poly(organophosphazenes). Synthesis, Unique Properties, and Applications H. R. Allcock
Proc. of 5th Internat. Symp. on Ring-Opening Polymerization, Blois, France, 1986

Makromol. Chem., Macromol. Symp. 1986, 6, 101-108.

The Organometallic Chemistry of Phosphazenes H. R. Allcock. J. L. Desorcie, and G. H. Riding Polyhedron 1987, 6, 119-157.

Polymerization of New Metallocenylphosphazenes H. R. Allcock, G. H. Riding, and K. D. Lavin Macromolecules 1987, 20, 6-10.

Synthesis and Characterization of the First Stable Cyanophosphazenes J. S. Rutt, M. Parvez, and H. R. Allcock J. Am. Chem. Soc. 1986, 108, 6089-6090.

The Synthesis and Structure of Transition Metal-Bound Phosphazenes Derived from Phosphazene Anions
H. R. Allcock, M. N. Mang, G. H. Riding, and R. R. Whittle
Organometallics 1986, 5, 2244-2250.

A Dibenzenechromium-Bridged Cyclophosphazene: X-Ray Structure Analysis of $N_3P_3F_4(n-C_6H_5)_2Cr$ G. H. Riding, M. Parvez, and H. R. Allcock Organometallics 1986, 5, 2153-2154.

Reactions of Ferrocenv1- and Ruthenocenylphosphazenes with Lithiometallocenes, and the X-Ray Structures of N₃P₃F₄(η -C₅H₄)₂Fe, [N₃P₃F_e{(η -C₅H₄)₂Fe}{(η -C₅H₄)-Fe(η -C₅H₅)}], 1,5-N₄P₄F₆(η -C₅H₄)₂Fe, and 1,5,3,7-N₄P₄F₄[(η -C₅H₄)₂Ru]₂H. R. Allcock, K. D. Lavin, G. H. Riding, R. R. Whittle, and M. Parvez Organometallics 1986, 5, 1626-1635.

A Bis-Transannular Metallocenyl Cyclophosphazene. X-Ray Crystal Structure of $N_4P_4F_4[(n-C_5H_4)_2Ru]_2$ K. D. Lavin, G. H. Riding, M. Parvez, and H. R. Allcock J. Chem. Soc., Chem. Commun. 1986, 117.

Conformation, Bonding, and Flexibility in Short-Chain Linear Phosphazenes H. R. Allcock, N. M. Tollefson, R. A. Arcus, and R. R. Whittle J. Am. Chem. Soc. 1985, 107, 5166-5177.

Ring-Opening Polymerization of Metallocene Cyclophosphazene Derivatives H. R. Allcock, K. D. Lavin, and G. H. Riding Macromolecules 1985, 18, 1340-1345.

Reactions between Hexachlorocyclotriphosphazene and Hexamethylcyclotrisiloxane: Polymerization, Ring Cleavage, and Crosslinking H. R. Allcock, D. J. Brennan, and R. W. Allen Macromolecules 1985, 18, 139-144.

Metal Exchange Reactions Under the Influence of a Cyclophosphazene Template: Iron, Cobalt, and Rhodium Metallophosphazenes
H. R. Allcock, P. R. Suszko, L. J. Wagner, R. R. Whittle, and B. Boso
Organometallics 1985, 4, 446-457.

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